

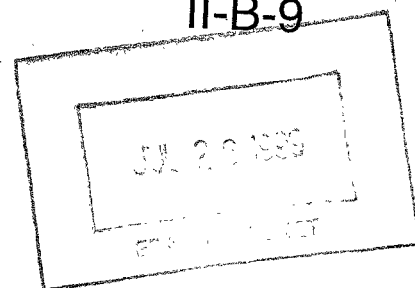


**ALPHA-GAMMA**

TECHNOLOGIES, INC.

A-95-35

II-B-9



**MEMORANDUM:**

**DATE:** August 1, 1996

**SUBJECT:** "Fourier Transform Infrared (FTIR) Method Validation" (for emission testing of natural gas fired RICE)

**FROM:** James Camp  
Alpha-Gamma Technologies, Inc.

**TO:** RICE NESHAP Project Files

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The Gas Research Institute funded a study to validate the FTIR method for quantifying aldehyde emissions from Stationary Reciprocating Internal Combustion engine (RICE) exhaust. Testing was conducted to validate the extractive FTIR method for measurement of formaldehyde, acetaldehyde, acrolein, NO<sub>x</sub>, CO, CO<sub>2</sub>, and water emissions from natural gas fired RICE. Analyte spiking was used to validate FTIR measurements of aldehydes while applicable EPA reference methods 7E, 3A, 10 and 4 were used to validate FTIR measurements of NO<sub>x</sub>, CO<sub>2</sub>, CO, and moisture, respectively. The procedures specified in EPA Method 301 (Field Validation of Pollutant Measurement Methods from Various Waste Media) were followed during testing.

The FTIR method is a real-time, automated method capable of measuring a variety of pollutant species in internal combustion engine exhaust streams. CARB Method 430 utilizes impingers immersed in a 2,4-dinitrophenylhydrazine (DNPH) solution (that is orange in color) and is suitable for measuring aldehyde concentrations collected from the exhaust streams of combustion sources. Aldehydes react with DNPH to form 2,4-dinitrophenylhydrazone. This reaction (or any other reaction which consumes DNPH) causes the impinger solution to go from orange to clear. Aldehyde emissions are determined by laboratory measurement of the 2,4-dinitrophenylhydrazone concentration in the impinger solution after CARB Method 430 sample collection is completed.

Simultaneous FTIR and CARB Method 430 emission testing of engines known (from previous testing) to emit measurable quantities of aldehydes was performed. For certain test runs, FTIR and field blank results both indicated significant aldehyde concentrations while impinger solutions, although clear, indicated no significant concentrations of aldehyde derivatives. These facts indicate that a potential cross reaction consumed the DNPH and contaminated the CARB Method 430 results. The GRI report contains a literature citation which suggests that potential interference may be caused by exhaust gas NO<sub>x</sub>.

The EPA, in a July 21, 1995, letter from William Hunt (EPA Emissions,

Monitoring and Analysis Division) to James McCarthy (GRI) stated that FTIR "can be considered valid for this source (a natural gas fired reciprocating internal combustion engine) and similar sources," and "may be used at any gas-fired (RICE)."

The CARB Method 430 procedures require that a target aldehyde concentration has to be selected (based on known or suspected aldehyde emission concentrations or based on applicable emission limits) prior to actual sampling. A sampling volume and sampling time are calculated based on this target concentration, to ensure that adequate reagent is present throughout the sampling period. The total quantity of aldehydes collected on an impinger during the collection period is calculated based on the quantity and concentration of reagent present at the start of the sampling period. Consequently, the variability of emissions during the test period cannot be determined using a single impinger. In addition, the method has not been validated for exhaust gas streams with high particulate or moisture loading. Use of steam or water injection techniques to reduce  $\text{NO}_x$  emissions from RICE is therefore likely to bias CARB Method 430 formaldehyde emission measurements (as is the presence of  $\text{NO}_x$  in the exhaust stream). The FTIR method is a real-time method of measuring exhaust components from their characteristic infrared spectrum by routing a portion of the exhaust stream directly into an infrared spectrometer.

The GRI report indicates three advantages of the FTIR method:

- 1) FTIR, unlike CARB Method 430, is an EPA validated method for emission testing of RICE exhaust;
- 2) FTIR method appears to be less susceptible to contamination; and
- 3) Engine  $\text{NO}_x$  or moisture emissions (water or steam injection reduces  $\text{NO}_x$ ) can bias CARB Method 430 results. Therefore, combustion sources producing  $\text{NO}_x$  or utilizing water based  $\text{NO}_x$  controls cannot be expected to be accurately monitored for aldehyde emissions according to CARB Method 430 procedures.